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## Organophosphate esters in indoor and outdoor dust from Iraq: Implications for human exposure



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### ABSTRACT

Concentrations of 6 organophosphate esters (OPEs) were determined in 60 indoor (ID) and outdoor (OD) dust samples collected from 20 homes from Basrah, Iraq. From each home, two ID samples were collected, one from elevated surfaces (ESD) and one from the floor (FD) of the living room; while the OD samples were collected from the front yard of the same house. Total  $\Sigma_6$ OPEs concentrations in dust samples ranged between 681 and 17900 ng/g with median concentrations of 5950, 3590 and 1550 ng/g in ESD, FD and OD samples, respectively. Chlorinated OPEs were the most abundant compounds, contributing mean percentages of 88%, 85% and 78% to  $\Sigma_6$ OPEs in ESD, FD and OD, respectively, with tris (1-chloro-2-propyl) phosphate (TCIPP) dominant. Concentrations of our target OPEs in ESD significantly exceeded those in FD ( $p < 0.05$ ) for tris (2-chloroethyl) phosphate (TCEP) and tris (1,3-dichloro-2-propyl) phosphate (TDCIPP). Ratios of median concentrations of OPEs in ID:OD ranged from 1.5 for tri-*n*-butyl phosphate (TNBP) to 8.0 for TCEP, indicating the significance of indoor sources. Concentrations of chlorinated OPEs in ID were moderately correlated ( $R = 0.522-0.591$ ,  $P < 0.05$ ) with those in OD samples, suggesting interchange of OPEs between the two environments. Concentrations of OPEs in OD from houses with a contiguous front yard car porch exceeded those in OD from houses without a car porch and were significantly higher ( $P < 0.05$ ) for TCEP, TCIPP and 2-ethylhexyl diphenyl phosphate (EHDPP). Emissions from parked cars and the associated home are likely sources of OPEs in the OD area. Based on the concentrations reported here, the estimated daily intake (EDI) for the Iraqi population through house dust ingestion are all well below the relevant reference dose (RfD) values.

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### 1. Introduction

Bans and restrictions on the manufacture and use of the main commercial brominated flame retardants (BFRs), have led to an increase in the production and use of alternative flame retardants (FRs), such as organophosphate esters (OPEs) [1,2] and “novel” brominated flame retardants (NBFRs) [3]. OPEs are a group of phosphoric acid derivatives containing either alkyl chain or aryl groups, and can be classified into halogenated and non-

halogenated compounds. Halogenated (chlorinated) organophosphate esters such as: tris (2-chloroethyl) phosphate (TCEP), tris (1-chloro-2-propyl) phosphate (TCIPP) and tris (1,3-dichloro-2-propyl) phosphate (TDCIPP) are commonly used as flame retardants added to polyurethane foam, textiles, furniture, electrical and electronic equipment, building materials, insulation materials and paints. While non-halogenated OPEs such tri-*n*-butyl phosphate (TNBP), tri-phenyl phosphate (TPHP) and 2-ethylhexyl diphenyl phosphate (EHDPP), are primarily used as plasticisers in anti-foam agents, lacquers, glues, floor finish waxes, hydraulic fluids, as well as flame retardants [4,5]. The global consumption of OPEs increased rapidly from 100,000 metric tons in 1992 to 500,000 metric tons in 2011 and to 680,000 metric tons in 2015 [6]. In 2019, OPEs represented the second largest global market share of flame retardants (18%), after aluminum hydroxide (38%), while brominated compounds and antimony oxide represented 17% and

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8.0%, respectively [7]. Asia Pacific is the largest FR market followed by North America, Europe, Middle East and Latin America, respectively [8].

Since OPEs are semi-volatile organic compounds and incorporated into goods as additives, they can be released from the treated products into the environment through volatilisation, abrasion and direct contact [4,9]. Consequently, they are globally distributed across a wide range of indoor and outdoor environments, such as surface water [10], sediments [11], soil [12], drinking water [13], foodstuffs [14], indoor air [15], outdoor dust [16,17] and indoor dust [18,19]. Additionally, OPEs have even been detected in the Arctic, suggesting long-range transport of these compounds to pristine areas [20,21]. Furthermore, several biomonitoring studies have detected OPEs in human biological samples such as: urine [22], hair [23], nails [24], serum [25], human milk [26] and human placenta [27], indicating their bioavailability [4].

Due to the probability of serious adverse health effects, OPEs have raised wide concern. Human exposure to OPEs may cause neurotoxicity [28], thyroid cancer [29], endocrine disruption [30], cardiotoxicity during embryogenesis [31], asthma and allergies [32,33], as well as poor foetal growth [34]. Consequently, they have been reported as a regrettable substitution for polybrominated diphenyl ethers (PBDEs) [2]. Significant correlations were found between concentrations of OPEs detected in indoor dust and their corresponding metabolites, suggesting that non-intentional dust ingestion is the main exposure source for such compounds [35–37].

Most previous assessments of exposure to chemical contaminants via dust ingestion have focused on floor dust only, even though significant differences in concentrations of such pollutants have been found between elevated surface and floor dust samples [32,38,39]. Thus, one type of dust sample (e.g. floor dust) may not represent a real estimate of exposure for *both* adults and toddlers [40]. While toddlers and young children are likely more exposed to floor dust, adults likely have far greater contact with dust from elevated surfaces, such as shelves, desks and table tops. From our previous studies regarding exposure assessment to BFRs, we concluded that sampling only floor dust may underestimate exposures, particularly for adults [41,42]. In addition, recent studies have shown notable concentrations of OPEs in outdoor dust, suggesting that both indoor and outdoor dust will be valuable for human risk assessments. OPEs in dust samples have been reported in a range of different outdoor environments, such as urban [43,44], e-waste recycling [16,45] and industrial areas [46]. However, to our knowledge, only two studies [17,47] have attempted to measure the concentrations of OPEs in paired indoor/outdoor dust samples from the same location. A significant correlation between the concentration of OPEs in paired indoor/outdoor dust samples suggested potential intermixing of these compounds between the two environments [17].

Despite abundant global studies on assessments of human exposure to OPEs via indoor dust ingestion, only a limited number have been performed in the Middle East [48–52]. To the best of our knowledge, this is the first report on OPEs in dust samples from Iraq. The study is designed to: (1) elucidate concentrations, profiles, and potential sources of three halogenated (TCEP, TCIPP, TDCIPP) and three non-halogenated (TNBP, TPHP, EHDPP) OPEs in Iraqi dust samples from paired indoor and outdoor environments; (2) explore within-room spatial variability of OPEs in dust samples taken from elevated surfaces and floor from the same microenvironment, as well as the relationship between concentrations of OPEs in house dust and dust from outdoor surfaces adjoining the sampled houses; and (3) provide the first preliminary evaluation of the exposure of the Iraqi population to OPEs in dust.

## 2. Materials and methods

### 2.1. Chemicals and standards

Standards of TCEP, TCIPP, TDCIPP, TNBP, TPHP, EHDPP,  $d_{12}$ -TCEP,  $d_{15}$ -TDCIPP and  $d_{15}$ -TPHP (50  $\mu\text{g}/\text{mL}$  in toluene) were purchased from Wellington laboratories, (Guelph, ON, Canada). TAP (triamyl phosphate; recovery determination standard) was purchased from TCI Europe (Zwijndrecht, Belgium). The purity of all analytical standards was >98%. Indoor dust SRM 2585 was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). All solvents and reagents (HPLC grade) were obtained from Fisher Scientific (Loughborough, UK). Florisil® SPE cartridges were purchased from Biotage (Uppsala, Sweden).

### 2.2. Sampling

In total, 60 indoor and outdoor dust samples were collected from 20 urban houses in Basrah province, South Iraq, from September to November 2019, during which period daily mean temperatures fall in the range 20–36 °C. Samples were collected using a vacuum cleaner (Dirt Devil DDMHH1-1100W) with a nylon sampling sock (25  $\mu\text{m}$  pore size) inserted into the nozzle. In each house, the following samples were collected: two indoor dust (ID) samples comprising one floor dust (FD) and one elevated surface dust (ESD) sample, along with one outdoor dust (OD) sample. Samples from the same house were all collected on the same day. FD samples were collected from the most frequently used floor areas in the main living room, according to a standardised protocol [53]. In brief, 4  $\text{m}^2$  of bare floor was vacuumed for 4 min, while for carpeted floors, 1  $\text{m}^2$  surface was vacuumed for 2 min. ESD were collected from available elevated surfaces (typically between 50 and 150 cm height from floor level) such as tables, shelves, and chairs in the same living area for 2–4 min [41]. OD samples were collected for 2–4 min by vacuuming available areas next to the wall and surfaces above the ground in the main house entrance area which represents the front yard of the house located between the house and the outer boundary of the property. In Basrah, these contiguous outdoor areas are often used as car parking areas or porches which sometimes have a roof. At the time of sampling, information on potential influences on OPE contamination were recorded, including: floor material, the number and type of putative OPE sources and type of car parking area (e.g. roofed porch) contiguous with the entrance of the house and house ventilation system (Table S1). After sampling, socks were closed, sealed in a plastic bag and stored at  $-20$  °C.

### 2.3. Sample preparation and analysis

Analysis of OPEs in dust samples was performed at the University of Birmingham, UK. Prior to analysis, all samples were sieved through a 125  $\mu\text{m}$  mesh size sieve, meaning that dust particles analysed in this study are in the range 25–125  $\mu\text{m}$  diameter. Accurately weighed aliquots of dust sample (around 75 mg) were spiked with 50 ng each of  $d_{12}$ -TCEP,  $d_{15}$ -TDCIPP and  $d_{15}$ -TPHP as internal standards and extracted with *n*-hexane: acetone (3:1, v/v) according to the method previously described [54]. Briefly, samples were extracted with 2 x 2 mL of hexane: acetone (3:1 v/v) (vortexed for 2 min, sonicated for 5 min) and centrifuged at 3500 rev/min for 5 min. This process was repeated three times and the pooled supernatants were collected, evaporated to incipient dryness, and resolubilised in 1 mL of hexane. The extract was fractionated into two fractions using Florisil cartridges. Fraction 1 was achieved by eluting with 8 mL of hexane, with fraction 2 (containing OPEs) eluted with 10 mL of ethyl acetate. Fraction 2 was evaporated to

incipient dryness under a gentle nitrogen stream and resolubilised in 100  $\mu\text{L}$  of isooctane containing 500  $\text{pg}/\mu\text{L}$  of TAP as recovery determination standard.

Analysis of OPEs was performed using a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS) operated in electron impact ionisation (EI) mode (both Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ), using helium as the carrier gas. 1  $\mu\text{L}$  of purified extract was injected on column. The inlet temperature was set at 50  $^{\circ}\text{C}$ . The GC oven temperature program was set at 50  $^{\circ}\text{C}$  for 0.5 min, ramp 15  $^{\circ}\text{C}/\text{min}$  to 250  $^{\circ}\text{C}$ , 40  $^{\circ}\text{C}/\text{min}$  to 300  $^{\circ}\text{C}$ , and 1  $^{\circ}\text{C}/\text{min}$ , hold 5 min. The ion source and interface temperatures were set at 290 and 300  $^{\circ}\text{C}$ , respectively.  $d_{12}$ -TCEP was used as internal standard for quantification of TNBP, TCEP and TCIPP.  $d_{15}$ -TDCIPP was used to quantify TDCIPP, and  $d_{15}$ -TPHP was used to quantify TPHP and EHDPP. Monitored  $m/z$  values and detailed information about the instrumental method can be found in Figs. S1 and S2.

#### 2.4. QA/QC

Two method blanks (i.e. where the dust sample is omitted) and one indoor dust standard reference material (SRM 2585) were analysed for each batch of 10 dust samples. Thus, in total, 12 method blanks and 6 aliquots of SRM 2585 were processed. In addition, 3 field blanks (comprising 0.20 g of pre-cleaned anhydrous sodium sulfate vacuumed with the vacuum cleaner, collected in a nylon sock, and treated as a dust sample) were also analysed to assess any contamination resulting from sampling, transport, and storage of samples. TNBP and chlorinated OPEs were detected in the method and field blanks such that the concentration of the target analyte was <11% of the lowest concentration in that batch. Thus, results were blank corrected (when the analyte concentration in the blank fell between 5.0% and 11%) by subtraction of mean blank values from the raw values of OPEs in the dust samples. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were performed as the amount of an analyte that yielded signal-to-noise ratios of 3 and 10, respectively. Where a target compound was detected in a blank, the LOQ for that analyte was calculated as the mean plus 3 times the standard deviation of the concentrations detected in the blank samples. This is called the Minimum Reported Value (MRV). LOD, LOQ and MRV values are provided in Table S2. The values of OPEs in SRM 2585 were in agreement with several recent published values [50,55–58] and certified values with percentage error ranged between 6 and 23, as listed in Table S3. Mean  $\pm$  standard deviation percent recoveries of internal standards in dust samples were: 83%  $\pm$  13, 72%  $\pm$  14 and 86%  $\pm$  17 for  $d_{12}$ -TCEP,  $d_{15}$ -TDCIPP and  $d_{15}$ -TPHP respectively.

#### 2.5. Exposure assessment

Concentrations of OPEs in this study were used to calculate preliminary estimated daily intake (EDI) values for the Iraqi population through house dust ingestion. Two plausible dust ingestion exposure scenarios were estimated using median and 95th percentile concentrations.

We used mean and high dust ingestion rates which have been recently updated by the United States Environmental Protection Agency [59] of 20 and 60  $\text{mg}/\text{day}$  for adults, and 50 and 100  $\text{mg}/\text{day}$  for toddlers, respectively. Assumed mean body weights were 80 kg for adults and 13.8 kg for toddlers [59,60]. Due to the lack of relevant empirical data, we have assumed 100% absorption of intake [61]. Due to unavailability of data on time-activity patterns for the

Iraqi population, our exposure estimates are based pro-rata to typical activity patterns reported previously [62] (for adults 64% home and 4.7% outdoors; for toddlers 86% home and 4.7% outdoors, with time spent in other locations not sampled in this study like offices, cars or public microenvironments making up the rest).

The algorithm given below was used to estimate both adult and toddler exposure to target OPEs via dust ingestion [58,63].

$$\text{EDI} = (\text{C}_{\text{dust}} \times \text{IR}_{\text{dust}} \times \text{AF}_{\text{gastro}} \times \text{HEF})/\text{BW}$$

where  $\text{C}_{\text{dust}}$  is the concentration of OPEs in dust samples ( $\text{ng}/\text{g}$ ),  $\text{IR}_{\text{dust}}$  is the dust ingestion rate ( $\text{mg}/\text{day}$ ),  $\text{AF}_{\text{gastro}}$  is the gastrointestinal absorption fractions (100%), HEF is the fraction of time spent at home and BW is the body weight (kg).

#### 2.6. Statistical analysis

Statistical analysis was performed using Excel (Microsoft Office 2019) and IBM SPSS statistics software (V. 20). Shapiro-Wilk testing revealed that concentrations of all our target OPEs were skewed. Therefore, all data were log-transformed prior to One-way Repeated Measures (ANOVA) and  $t$ -test as appropriate for testing significant differences between arithmetic means. For the purposes of statistical evaluation, all concentrations below LOQ were assigned a value of 0.5 LOQ. Potential correlations between various parameters were investigated using Pearson's Correlation. Results were considered significant where  $P$  values were less than 0.05.

### 3. Results and discussion

#### 3.1. Levels and profiles of OPEs in Iraqi dust samples

Descriptive statistics for OPEs in ID (both ESD and FD) and OD samples from Basrah, Iraq are summarized in Table 1. Except for TNBP and TCEP in OD (in which the detection frequency was 95%), the detection frequency of our target OPEs in ESD, FD and OD samples was 100%. The highest  $\Sigma_6\text{OPEs}$  concentrations were observed in ESD samples which ranged from 2980 to 17900  $\text{ng}/\text{g}$  with a median of 3950  $\text{ng}/\text{g}$ , followed by FD and OD samples with medians of 3590 and 1550  $\text{ng}/\text{g}$ , respectively. As shown in Table 1, the OPE pattern was dominated by chlorinated OPEs, ESD (88%), FD (85%) and OD (78%). Among the 6 OPEs studied, TCIPP was the

**Table 1**

Statistical summary of concentrations ( $\text{ng}/\text{g}$ ) of target OPEs in elevated surface dust (ESD), floor dust (FD), and outdoor dust (OD) from Iraqi homes ( $n = 20$ ).

	TNBP	TCEP	TCIPP	TDCIPP	TPHP	EHDPP	$\Sigma\text{OPEs}$
<b>Elevated Surface dust (ESD)</b>							
Mean	94.6	1660	3530	1080	384	346	7080
Median	75.8	1250	2310	742	346	194	5950
Min	26.5	371	630	183	101	47.3	2980
Max	279	4500	14600	2870	754	2730	17900
DF <sup>a</sup> %	100	100	100	100	100	100	100
<b>Floor Dust (FD)</b>							
Mean	88.4	865	1860	545	278	218	3860
Median	65.2	824	2250	507	227	220	3590
Min	19.8	90.0	247	39.3	46.0	37.0	1120
Max	368	2460	4170	1680	1070	389	6900
DF%	100	100	100	100	100	100	101
<b>Outdoor Dust (OD)</b>							
Mean	59.0	209	855	438	158	204	1920
Median	49.2	151	637	239	134	91.3	1550
Min	<DL	<DL	241	71.3	15.6	11.5	681
Max	157	791	2990	1700	588	1220	3830
DF%	95	95	100	100	100	100	100

<sup>a</sup> Detection frequency.



predominant compound, with mean percentage contributions to  $\Sigma_6$ OPEs of 50%, 48% and 44% in ESD, FD and OD dust samples, respectively. TCEP was the next most abundant, with mean contributions of 23%, 22% and 11%, followed by TDCIPP, 15%, 14% and 23% in ESD, FD, and OD dust, respectively. TNBP made the lowest mean percentage contribution in all dusts (1.3%, 2.3% and 3.1% in ESD, FD and OD, respectively). Fig. 1 depicts distribution profiles of OPEs in the three types of dust studied, with concentrations of OPEs in all dust samples provided in Tables S4, Tables S5 and Tables S6. Concentrations of  $\Sigma_6$ OPEs in Iraqi dust samples were approximately one order of magnitude higher than those of PBDEs reported in our previous study from Basrah, Iraq that analysed samples collected in 2013 [41]. This is possibly a result of the global phasing out of PBDEs, coupled with wide application and extensive use of OPEs as flame retardants and plasticisers in polyurethane foam, textiles, carpet padding, PVC, building materials and paints [4,64–66], as well as in vehicles [67].

### 3.2. Comparison with other studies

Although OPE concentrations in floor dust from Iraqi households are lower than those in domestic floor dust from the UK [67], USA [68,69], Canada [51,69,70] and Japan [32]; they are an order of magnitude higher than those from Egypt [50–52], Pakistan [48], Nepal [71] and across the mainland [17] and Wuhan City [72] in China. Concentrations of OPEs in the present study were comparable to those reported in Kazakhstan [18], Saudi Arabia [49] and several European countries, such as Italy, Belgium, Spain [58], Norway [38], Finland [73] and the Czech Republic [69]. In terms of the distribution pattern, our finding that TCIPP is the most abundant target OPE, is consistent with those in indoor dust from China [17,63], UK [67], Germany [18], Italy, Spain [58], Kuwait [48] and Saudi Arabia [49]. This contrasts with the pattern observed in

indoor dust in Canada [18], USA [68] and Brazil [74], where TPHP was the most abundant compound. This may be attributed to the presence of TPHP as one of the components of several product such as Firemaster 550 flame retardant marketed as a penta-BDE replacement in polyurethane foam in the USA [68,75]. To the best of our knowledge OPEs are not produced in Iraq, and we thus assume the sources of these pollutants are imported consumer products. Fig. 2 shows a comparison of concentrations of OPEs detected in FD with those from selected other studies. Further details (ng/g OPE concentrations, sampling date, dust particle size, and number of dust samples) of the selected studies are listed in Table S7.

### 3.3. Within-room vertical spatial variability of OPEs in dust samples between ESD and FD

A paired *t*-test was performed to evaluate within-room (between ESD and FD) spatial variability in concentrations of our target OPEs. The results revealed that except for EHDPP, (for which median concentrations were 194 and 220 ng/g in ESD and FD respectively); median concentrations of individual OPEs in ESD exceeded those in FD and significantly so for TCEP ( $p = 0.022$ ) and TDCIPP ( $p = 0.035$ ). Of note, median concentrations of TCEP, TDCIPP and TPHP, in ESD exceeded those in FD by a factor of 1.5. These findings are consistent with those of other studies in Japan [32,39], and Norway [38,76], who reported concentrations of OPEs in ESD to significantly exceed those in FD. Moreover, a significant correlation between OPE concentrations in ESD and FD was observed for TDCIPP ( $r = 0.732$ ,  $p < 0.001$ ) and TPHP ( $r = 0.451$ ,  $p = 0.046$ ), suggesting that sources of these contaminants in ESD and FD are similar.

As semi-volatile organic compounds (SVOCs) and additive chemicals, OPEs can be released from the treated products into the environment via volatilisation and subsequent sorption to dust depending on their vapour pressures ( $V_p$ ) and octanol-air partition coefficient ( $K_{OA}$ ) [77]. However, transfer via direct source:dust contact and abrasion of particles/fibres of treated materials have been demonstrated to make a greater contribution for BFRs [78,79]. In the present study, most ESD samples were collected directly from sofas, shelves and tables with electronic devices. From our previous meta-analysis [40] we identified several factors influencing the differences in concentrations of contaminants like OPEs in ESD and FD, including: a) differences in the number and type of putative sources present on floors and elevated surfaces, b) differences in dust particle size distribution between ESD and FD, c) the influence of outdoor particles such as sand and soil tracked indoors with footwear that likely dilute contaminant concentrations in FD and d) the likely less frequent cleaning of elevated surfaces than floors [40].

### 3.4. Differences in concentrations of OPEs in indoor and outdoor dust from the same homes

A one-way repeated measures ANOVA test revealed that concentrations of our target OPEs in both ESD and FD samples exceeded those in OD samples from the same homes and significantly so ( $p < 0.05$ ) for all six OPEs in ESD and for TCEP ( $p < 0.000$ ), TCIPP ( $p = 0.002$ ), TPHP ( $p = 0.028$ ) and EHDPP ( $p = 0.039$ ) in FD. In addition, paired *t*-test results revealed that concentrations of our target compounds in ID (expressed as the mean of concentrations detected in ESD and FD) were significantly higher ( $p < 0.000$ ) than those in OD samples from the same home. The median concentration ratios of OPEs in ID and OD samples were 1.5, 8.0, 3.7, 2.7, 2.4, 2.5 and 3.2, for TNBP, TCEP, TCIPP, TDCIPP, TPHP and EHDPP, respectively. These findings are consistent with two previous

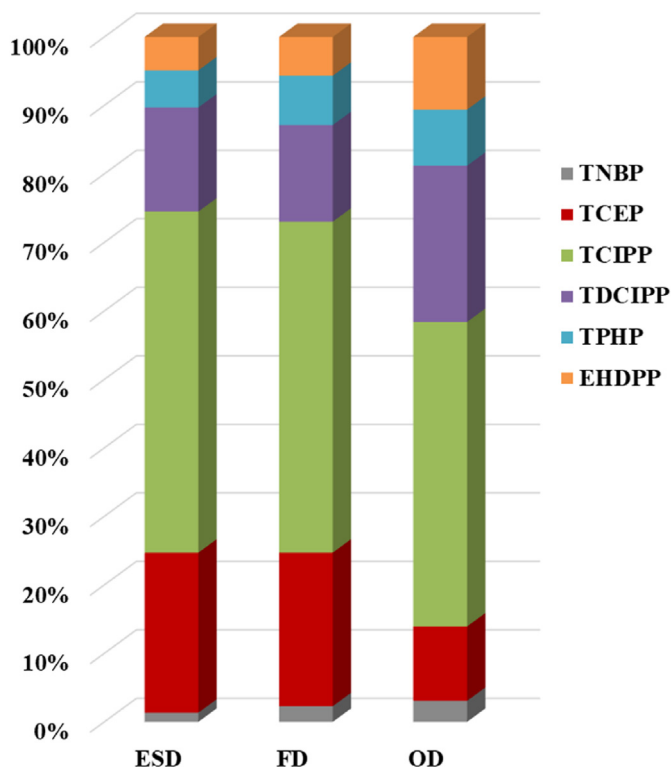
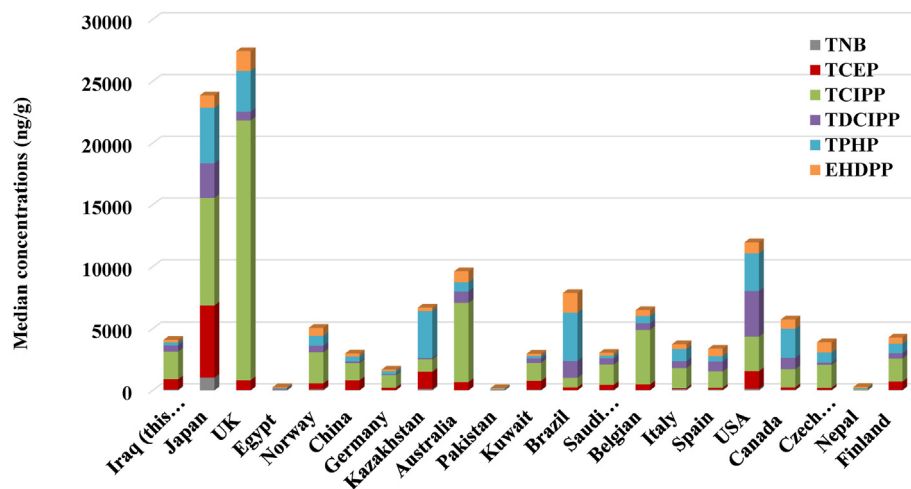


Fig. 1. Profiles and mean % contribution of target compounds to  $\Sigma_6$ OPEs in elevated surface dust (ESD), floor dust (FD) and outdoor dust (OD) samples from Iraqi homes.



**Fig. 2.** International comparison of selected concentrations and profiles of OPEs in floor dust samples from Iraq and those from other countries (Japan [32], UK [67], Egypt [50], Norway [38], China [63], Germany, Kazakhstan [18], Australia [87], Pakistan, Kuwait [48], Brazil [74], Saudi Arabia [49], Belgian, Italy and Spain [58], USA, Canada and Czech Republic [69], Nepal [71] and Finland [73]).

studies [17,47] that investigated OPEs in paired indoor/outdoor dust samples, that revealed concentrations of OPEs in indoor dust to exceed significantly by a factor of 7 those in outdoor dust in China [17], and to be twice as high in ID than OD in Pakistan [47]. Such observations of ID:OD ratios  $>1$ , suggest indoor sources may contribute significantly to concentrations of OPEs in outdoor environments. In addition, FRs in the outdoor environment may undergo photolytic and thermal degradation more readily than in indoor environments [47,80]. Thus, the notably high ratio for TCEP (8.0) suggests a combination of greater indoor source strength (TCEP has a greater vapour pressure than all our other target OPEs except TNBP and may thus volatilise more readily from indoor products), and greater susceptibility to photolytic and thermal degradation outdoors for TCEP. The Pearson correlation coefficients revealed that concentrations of the three chlorinated OPEs in our Iraqi FD samples were significantly ( $p < 0.05$ ) correlated with those in OD, with respective correlation coefficient values of 0.522, 0.589, 0.592 for TCEP, TCIPP and TDCIPP, respectively. This implies potential intermixing of OPEs in paired ID/OD dust from the same location by traffic on shoes and by transport through windows and doors [47,81].

It has been indicated that FRs migrate from products into indoor dust via three mechanisms which are: (1) sorption to dust particles after volatilisation from treated products, (2) physical transfer via abrasion from products in the form of particles or/and fibres, and (3) direct contact between dust and the surface of products [4,9]. To investigate to what extent sorption to dust particles after volatilisation may influence concentrations of our target compounds, scatter plots of  $\text{Log } K_{\text{OA}}$  versus ESD/FD and ID/OD mean ratios were used. As shown in Fig. 3A and B, such plots of ESD/FD and ID/OD mean ratios vs  $\text{Log } K_{\text{OA}}$  yielded R values of 0.16 and  $-0.57$  respectively. The relationship between  $K_{\text{OA}}$  and ESD/FD is clearly insignificant, suggesting that differences between OPE concentrations in ESD and FD are driven by other factors such as the particle size range. While the negative relationship between  $K_{\text{OA}}$  and ID/OD is also not significant, the R value is much greater. A possible explanation is thus. Assuming the same strength of OPE emission sources and that outdoor temperatures are higher than those indoors (as was the case in our study during the sampling period); one would expect greater partitioning of OPEs to ID than OD. This would be more marked for more volatile OPEs and thus ID/OD mean ratios would be expected to decrease with increasing  $K_{\text{OA}}$ . However, in

our study the ID/OD ratio for TCEP (point b in Fig. 3B) exceeds that for TNBP (point a in Fig. 3B), despite these two OPEs having near identical  $K_{\text{OA}}$  values. We believe here that the  $K_{\text{OA}}$  relationship is overridden by a greater indoor source strength for TCEP (as indicated by the much higher concentrations of TCEP than TNBP). Overall therefore, we believe our study provides suggestive (but not conclusive) evidence that volatilisation followed by sorption to dust is likely the predominant pathway via which OPEs migrate from products to dust.

While based on a small number of homes (20), available data allowed us to investigate the factors influencing concentrations of OPEs in OD samples. The front yards of the investigated homes were categorised as either: an area (with a shelter) that is intended for parking vehicles, or a non-parking area. Concentrations of OPEs in OD samples from houses where the front yard was used for car parking, exceeded those in OD from other homes; with a paired  $t$ -test revealing this difference to be significant for TCEP, TCIPP and EHDPP with  $p$  values of 0.00313, 0.0205 and 0.0224, respectively. The elevated concentrations of OPEs in OD samples from houses with front yards used for car parking may indicate vehicles as potential emission sources [82]. Several studies have reported high concentrations of OPEs in car dust, with chlorinated OPEs dominant [48,50,67,83]. This is probably due to the use of Cl-OPEs in rigid and flexible polyurethane foams, rubbers and paint [1,84]. Interestingly, in one house (H2; Table S6), the concentration of EHDPP (1220 ng/g) in OD exceeded that in ID (mean of ESD and FD) by a factor of 4.2. In this house, in addition to the use of the front yard for car parking, a large number of car spare parts were present in the front yard. The house in question was also located on a main road with high traffic sources. It is likely that OPEs in our OD samples arise from a mix of road dust vehicular traffic emissions, indoor sources and emissions from any cars parked in the front yard.

### 3.5. Human exposure to OPEs via dust ingestion

Table 2 summarises the EDIs of both adults and toddlers to OPEs via dust ingestion under various exposure scenarios. EDIs of  $\Sigma_6\text{OPEs}$  assuming median concentrations in dust and mean dust ingestion rates were between 0.0182 (assuming ingestion of OD only) and 0.950 (assuming ingestion of ESD only) and 0.264–18.6 ng/kg bw/day for adults and toddlers respectively. Assuming high dust ingestion rates of dust contaminated at the median concentration,

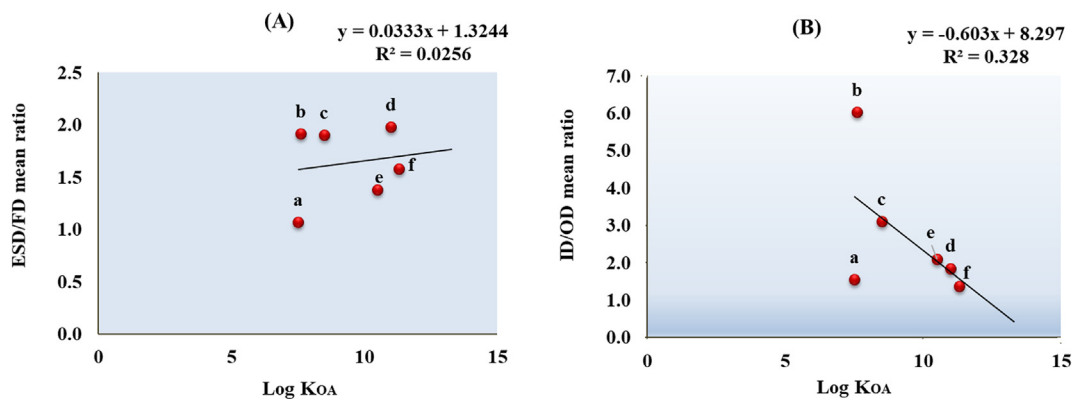


Fig. 3. The relationship between ESD/FD and ID/OD mean ratios vs Log  $K_{OA}$  of OPEs (TNBP, TCEP, TCIPP, TDCIPP, TPHP and EHDPP represented by a, b, c, d, e, and f respectively).

Table 2

Estimates of Exposure (ng/kg body weight/day) of Adults and Toddlers of OPEs via Dust Ingestion in Iraq.

OPE	RfD* values [63]	ESD				FD				OD			
		Adults		Toddler		Adults		Toddler		Adults		Toddler	
		Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile	Median	95th %ile
<b>Mean dust ingestion</b>													
TNBP	24000	0.0121	0.0348	0.236	0.681	0.0104	0.035	0.203	0.676	0.000578	0.00177	0.00838	0.0256
TCEP	22000	0.200	0.603	3.91	11.8	0.131	0.320	2.57	6.25	0.00178	0.00612	0.0257	0.0887
TCIPP	80000	0.369	1.579	7.22	30.88	0.359	0.507	7.02	9.91	0.00748	0.0270	0.108	0.392
TDCIPP	15000	0.118	0.351	2.32	6.86	0.0809	0.207	1.58	4.04	0.00281	0.0184	0.0407	0.267
TPHP	70000	0.0552	0.113	1.08	2.20	0.036	0.122	0.710	2.39	0.00157	0.00546	0.0228	0.0791
EHDPP	n.a.	0.0309	0.145	0.605	2.84	0.035	0.055	0.686	1.08	0.00107	0.00595	0.0156	0.0863
$\Sigma$ OPEs		0.950	2.61	18.6	51.0	0.573	1.09	11.2	21.4	0.01820	0.0431	0.264	0.624
<b>High dust ingestion</b>													
TNBP	24000	0.0363	0.104	0.473	1.36	0.0312	0.104	0.407	1.35	0.00173	0.00530	0.0168	0.0512
TCEP	22000	0.599	1.81	7.82	23.6	0.394	0.959	5.14	12.5	0.00533	0.0184	0.0515	0.177
TCIPP	80000	1.11	4.74	14.4	61.8	1.08	1.52	14.0	19.8	0.0225	0.0811	0.217	0.784
TDCIPP	15000	0.355	1.05	4.63	13.7	0.243	0.620	3.16	8.08	0.00843	0.0553	0.081	0.534
TPHP	70000	0.166	0.338	2.16	4.41	0.109	0.367	1.42	4.78	0.00472	0.0164	0.0456	0.158
EHDPP	n.a.	0.0928	0.435	1.21	5.67	0.105	0.166	1.37	2.17	0.00322	0.0179	0.0311	0.173
$\Sigma$ OPEs		2.85	7.82	37.1	102	1.72	3.28	22.4	42.8	0.0546	0.129	0.528	1.25

EDIs increased to a range of 0.0546–2.58 and 0.528–37.1 ng/kg bw/day for adults and toddlers respectively. At worst case scenarios (assuming high dust intake and 95th percentile OPE concentrations), EDIs for adults and toddlers were 7.82 (assuming ingestion of ESD only), and 42.8 (assuming ingestion of FD only), and 0.129 and 1.25 ng/kg bw/day (assuming ingestion of OD only), respectively.

Due to their lower body weight and greater assumed dust ingestion rate, EDIs for toddlers exceed those of adults by factors of 10–20. However, toddler exposure via dust ingestion based on ESD alone, is very likely an overestimate as they are more likely to ingest floor dust, while adults are more likely to ingest ESD (Al-Omran and Harrad, 2016). Our exposure estimates of OPEs for the Iraqi population are comparable with those calculated for Sweden [68], Germany [85], China [63], South Korea [86], Saudi Arabia [49] and Kuwait [48]. In turn, they are lower than those reported for the UK [67], Brazil [74] and Australia [87] by factors of 2.2, 13.4 and 1.4 for adults and 6.4, 10.5 and 2.9 for toddlers respectively. On the other hand, our exposure estimates exceeded those for Pakistan [48] and Nepal [71] by factors of 3.3 and 4.6 for adults and 4.1 and 9.2 for toddlers respectively. Reassuringly, for both adults and toddlers, the EDIs of individual OPEs in the present study are several orders of magnitude lower than reference dose values [63,85]. However, exposure via other pathways such as the diet and dermal contact with OPE-treated materials that may erode that margin of safety should be considered in further exposure assessments [88].

#### 4. Conclusion

To the best of our knowledge, this is the first study to document concentrations and profiles of OPEs in Iraqi dust samples. While we acknowledge the relatively small sample size of this study to potentially limit the extent to which our data represent Iraq as a whole; in general, concentrations of OPEs in Iraqi dust were comparable or lower than those reported elsewhere in the world. In line with other studies from Europe, China, Kuwait and Saudi Arabia, the OPE contamination pattern observed in this study revealed TCIPP as the most abundant compound; though this contrasts with North America and Brazil, where TPHP predominates. Except for EHDPP, concentrations of OPEs in ESD exceed those in FD and significantly so for TCEP and TCIPP. Thus, particularly for adults, caution must be exercised when exposure assessment is calculated based on floor dust only, as they are more likely to ingest ESD more than FD. While this study revealed considerable concentrations of OPEs in outdoor (front yard) dust, these are significantly lower than those in matched indoor house dust samples. Our finding that OPE concentrations in dust from front yards are significantly higher when these are used for car parking, suggests that vehicles are significant sources of OPEs and further investigation of this is recommended. While estimates of exposure to our target OPEs via dust ingestion for the Iraqi population reassuringly fall well below existing health-based reference dose values, our study does not account for exposures via dust ingestion outside the home, nor

other likely important pathways like inhalation, diet, and dermal uptake from OPE-treated goods. Comprehensive assessment of population exposure via all pertinent pathways is recommended.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2021.10.003>.

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